THE SYNTHESIS AND ANALYTICAL APPLICATIONS OF 1,10-PHENANTHROLINE DERIVATIVES

BY

FREDERIC PAUL RICHTER

A.B., Temple University, 1936

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS,

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THE SYNTHESIS AND ANALYTICAL APPLICATIONS OF 1,10-PHENANTHROLINE DERIVATIVES

INTRODUCTION

The study of new derivatives of 1,10-Phenanthroline was suggested by the need for extending the applicable potential range of the ferroin indicators.

Procedures for the colorimetric estimation of iron by means of 1,10-Phenanthroline have been described,[1,2,3] and the use of new derivatives affords the possibility of increasing the pH range and sensitivity.

A third application of these derivatives is the use of their ferrous complexes as qualitative analytical reagents.

The main purposes of the present study are:

A. To develop suitable methods for the synthesis, isolation and purification of new 1,10-Phenanthroline derivatives.

B. To determine the formal oxidation-reduction potentials of the newly synthesized ferroins in various concentrations of sulfuric acid.

C. To measure the absorption spectra of solutions of the substituted ferroins in order to predict the possible application of the 1,10-Phenanthroline derivatives as colorimetric reagents for iron.

D. To determine semi-quantitatively the solubilities of various ferroin and substituted ferroin salts with the purpose of predicting the possible applications of the ferroins as qualitative analytical reagents.

EXPERIMENTAL

A. The 5-methyl, 5-chloro and 5-bromo-(1,10)-Phenanthrolines were synthesized by applying the Skraup reaction to the corresponding 6-methyl, 6-chloro and 6-bromo-8-aminoquinolines. A general procedure was developed employing the mass relations: 1 mole of the amine, 4 moles of dry glycerol, 0.75 mole of As_2O_5 and a weight of sulfuric acid equal to 50-60 per cent of the weight of glycerol used. The mixture was kept at 130° for one hour and then held in active reflux for six more hours. The product was obtained, after dilution and neutralization of the reaction mixture, by extraction with boiling benzene. Purification was effected by distillation *in vacuo* and/or recrystallization from chloroform or a petroleum ether-benzene solvent mixture. The monopicrates were prepared as confirmatory derivatives.

The 5-nitro and 5-nitro-6-methyl derivatives were obtained by direct nitration.

B. The apparatus employed was the same as that used and described by Smith and Getz.[4] The differential titration method described by Walden, Hammett and Edmonds[5] was applied to the substituted ferroins wherever these were sufficiently stable. The ferrous-ferric system was used as the low, and the dichromate-chromic system as the high potential reference point. In the case of methyl-ferroin the method was satisfactory only in 4 formal sulfuric acid solution because of the change in the potential of the indicator system with change in the acid concentration.

In the higher acid concentrations the complexes of higher potential decompose too rapidly to allow the use of the titrational method. A general procedure was devised which involved the preparation of a solution containing equivalent amounts of the oxidized and reduced forms. The potential was recorded directly.

The values of the single formal potentials in 0.5 to 8 formal sulfuric acid are given in the table. In the cases of ferroin and methyl- ferroin the potentials given are the average of those found by both methods. These values agree within the experimental error of ± 0.02 volt. Potentials not listed in the table in the higher acid concentrations could not be measured because of the insolubility of the complex sulfates.

THE SINGLE ELECTRODE POTENTIALS OF VARIOUS FERROIN INDICATOR SYSTEMS IN 0.5 TO 8 FORMAL SULFURIC ACID SOLUTION

(In volts, referred to the Normal Hydrogen Electrode)

Indicator	Sulfuric Acid Concentration						
	0.5 F	F	2 F	3 F	4 F	6 F	8 F
Nitro-Ferroin	1.26	1.25	1.22	.....	1.17	1.12	1.11
Nitro-Methyl-Ferroin	.....	1.23	.....	.....	.....	.....	.....
Bromo-Ferroin	1.13	.....	.....	.....	.....	.....	.....
Chloro-Ferroin	.....	1.11	1.10	.....	1.04	0.97	.....
Ferroin	.....	1.06	1.03	1.00	0.96	0.89	0.76
Methyl-Ferroin	.....	1.02	1.00	0.96	0.93	0.86	0.70
2,2′-Bipyridyl Ferrous	.....	0.97	.....	.....	0.92	.....	.....

C. The absorption spectra of ferroin and the methyl, chloro, bromo, nitro and nitro-methyl derivatives in N/5000 solution were determined over the wave length range of 400-700 millimicrons. A General Electric Hardy recording spectrophotometer was used.

*D. Sixty anions were included in the study. Equal quantities of 0.01 N. anion and of 0.01 N. ferroin, or substituted ferroin solutions, were mixed. The filtrate, which contained any dissolved ferroin salt was compared visually with a series of standard ferroin and substituted ferroin solutions. Thus a measure of the solubility was obtained. The tests were repeated, using a 100 per cent excess of the reagent and a 100 per cent excess of the anion.

DISCUSSION

A. The synthesis of 1,10-Phenanthroline and its 5-substituted derivatives from the corresponding 8-aminoquinoline is much more satisfactory than from the 1,2-phenylene diamine, due to the anomolous behavior of the latter in undergoing the Skraup reaction.[6] The identity of the 5-bromo derivative obtained in the present study from 6-bromo-8-aminoquinoline was established by analysis, chemical properties and comparison of its absorption spectra with those of the parent base. This proves that the reported synthesis[7] of this compound from 4-bromo-1,2-phenylene diamine is incorrect.

The 5-chloro-1,10-Phenanthroline synthesized from 6-chloro-8-aminoquinoline was identical with that reported by Kuczynski and Sucharda,[8] presumably obtained from 5-chloro-8-aminoquinoline. This suggests a symmetrical bond structure by establishing the identity of the 5 and 6 positions in 1,10-Phenanthroline.

B. The effect of the acid concentration upon the potentials of the ferroin and substituted ferroins is not explained by the simple indicator mechanism:

$$Fe(C_{12}H_8N_2)_3^{+++} + e = Fe(C_{12}H_8N_2)_3^{++}$$

A new mechanism is postulated to explain this, and the effect of substituent groups upon the observed potential:

(1) $\underset{Red}{Fe(C_{12}H_8N_2)_3^{++}} + 6H^+ = Fe^{++} + 3(C_{12}H_8N_2H_2)^{++}$

(2) $Fe^{++} = Fe^{+++} + e$

(3) $(C_{12}H_8N_2H_2)^{++} = C_{12}H_8N_2 + 2H^+$

(4) $x(C_{12}H_8N_2) + Fe^{+++} =$ Blue Complex of Unknown Structure.

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* The experimental part, (D), was carried out by W. H. Taylor.[9]

The Nernst expression, $E = E_0 + RT/F \ln Fe^{+++}/Fe^{++}$, is applied to the equilibrium (2), the concentrations of the Fe^{++} and Fe^{+++} being determined by the equilibria (1) and (4). Increasing the H^+ concentration increases the Fe^{++} concentration more so than that of the Fe^{+++}. The latter when substituted in the Nernst expression result in a decrease in the observed potential E. This agrees with experiment.

The nitro, bromo and chloro groups lower the basicity of the phenanthroline which results in the equilibrium (1) lying farther to the left. This gives a lower Fe^{++} concentration and an increase in the observed potential E. The methyl group has the opposite effect upon the basicity of 1,10-Phenanthroline and by the same reasoning methyl ferroin has a lower potential than ferroin. In the case of the nitro-methyl derivative the substituent groups are opposing in their effects, but these effects are additive within the experimental error of measurement.

C. The absorption spectra of all the ferroin and substituted ferroin solutions are quite similar so that any of the substituted phenanthrolines studied could be used as colorimetric iron reagents. The nitro derivative has a somewhat more intense color which might be of advantage in its use as a colorimetric reagent. Since methyl ferroin is less readily decomposed in acid solution than ferroin, the use of methyl phenanthroline as a colorimetric reagent for iron would probably enable a wider pH range of application.

D. Studies of the solubilities of the ferroin salts indicate that a variety of tests for anions can be made with these reagents if combinations are used. The numbers of anions which are precipitated by the various ferroins indicate that the qualitative analytical properties of these reagents are determined not only by their molecular weight but by the nature of the substituent groups.

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VITA

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In September, 1932, he entered Temple University and was awarded a Beury Special Scholarship for the following four years. He received the degree of Bachelor of Arts with distinction in Chemistry in June, 1936, and was appointed graduate assistant in chemistry for the next two years at the same University. He received the degree of Master of Arts in June, 1938.

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